Preparation and Enrichment of Samarium Endohedral Fullerenes

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A graphite anode packed with a powder mixture of Sm_2Co_{17}, SiC, and graphite with a high atomic ratio of Sm/C was vaporized by direct current arc discharge under improved conditions including high helium pressure, low electric current, and wide electrode gap. The soot produced was successively extracted by CS_2 and pyridine, and the extracts were processed through column chromatography on silica gel. Matrix-assisted laser desorption−ionization time-of-flight (MALD-TOF) mass spectrometry analysis indicated that a high yield of samarium endohedral fullerenes ($Sm@C_{2n}$) with $Sm@C_{84}$ as the most abundant one was achieved. Possible reasons leading to this high yield are discussed.

Introduction

Since the report of the first extraction of metallofullerenes,[1] an intense effort has been made on the preparation, isolation, and characterization of these species. To date, many endohedral metallofullerenes have been isolated by HPLC and characterized by spectroscopic and structural analyses.[2−8] However, there have been fewer investigations on Sm endohedral fullerenes[9,10] than on those of the other rare earth's because of their very low production yield.[11,12] In fact, studies on Sm endohedral fullerenes should be meaningful in theory as well as potential applications. Samarium has an electronic configuration of $(Xe)^{54}(4f)^6(6s)^2$ with +3 oxidation state in classical chemistry. However, samarium ion trapped in carbon cages is assumed to have +2 oxidation state.[10] Then a question arises as to why Sm^{2+} is more stable than Sm^{3+} in the fullerene cages. On the other hand, since Sm-doped compounds usually have excellent luminescent properties,[13] $Sm@C_{2n}$ might be a novel optical material.

Endohedral metallofullerenes are conventionally synthesized either by the laser-ablation method, being helpful for investigations on the growth mechanism, or by the direct current (dc) arc discharge method, being beneficial to large-scale production. In a typical dc arc discharge method, a graphite rod loaded with metal or its oxide is vaporized by high-current arc in a He environment at low pressure. Up to the present, all of the rare earth metallofullerenes except those of the radioactive element Pm have been synthesized and the Sm metallofullerenes are the only ones that have not been isolated yet because of the low production yield. In this paper, we report a high-yield production of $Sm@C_{2n}$ under improved dc arc discharge conditions including high helium pressure, with Sm_2Co_{17} alloy as metal source, a high atomic ratio of M/C, a low electric current, and a large gap distance between electrodes. The soot produced was extracted successively by CS_2 and pyridine, and pyridine was found to be an excellent solvent for extracting Sm metallofullerenes. Moreover, column chromatography on silica gel was initially used to enrich the metallofullerenes, and a high content of Sm metallofullerenes suitable for further HPLC isolation was obtained.

Experimental Section

The raw soot was prepared by a dc arc discharge method under novel conditions. The anode is a o.d. 6 × 150 mm Specpure graphite rod with a drilled o.d. 4 × 120 mm hole, filled with a powder mixture of graphite, SiC and Sm_2Co_{17} alloy (at a C:Si:Sm molar ratio of 10:1:1). The cathode is a o.d. 10 mm specpure graphite rod with a tapered end pointing to the anode to lessen the formation of deposit. An arc was generated at 50 A in 720 Torr helium static atmosphere, while the gap between the anode and cathode was kept at about 12 mm by adjusting the anode forward. Usually, it took 1.5 h for a 12 cm consumption of the anode rod, and 4.5 g of soot with 0.5 g

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(1) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. F.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.

(2) Weaver, J. H.; Chai, Y.; Kroll, G. H.; Jin, C.; Ohno, T. R.; Haufler, R. E.; Guo, T.; Alford, J. M.; Conceicao, J.; Chibante, L. P. F.; Jain, A.; Palmer, G.; Smalley, R. E. *Chem. Phys. Lett.* **1992**, *190*, 460.

(3) Soderholm, L.; Wurz, P.; Lykke, K. R.; Parker, D. H.; Lytle, F. W. *J. Phys. Chem.* **1992**, *96*, 7153.

(4) Hasegawa, Y.; Ling, Y.; Yamazaki, S.; Hashizume, T.; Shinohara, H.; Sakai, A.; Pickering, H. W.; Sakurai, T. *Phys. Rev. B* **1997**, *56*, 6470.

(5) Seifert, G.; Bartl, A.; Dunsch, L.; Ayuela, A.; Rockenbauer, A. *Appl. Phys. A* **1998**, *66*, 265.

(6) Takata, M.; Umeda, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46.

(7) Yamamato, E.; Tansho, M.; Tomiyama, T.; Shinohara, H.; Kawahara, H.; Kobayasshi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2293.

(8) Lebedkin, S.; Renker, B.; Heid, R.; Schober, H.; Rietschel, H. *Appl. Phys. A* **1998**, *66*, 273.

(9) Gillan, E. G.; Yeretzian, C.; Min, K. S.; Alvarez, M. M.; Whetten, R. L.; Kaner, R. B. *J. Phys. Chem.* **1992**, *96*, 6869.

(10) Moro, L.; Ruoff, R. S.; Becker, C. H.; Lorents, D. C.; Malhotra, R. *J. Phys. Chem.* **1993**, *97*, 6801.

(11) Sun, D.; Liu, Z.; Guo, X.; Xu, W.; Liu, S. *J. Phys. Chem. B* **1997**; *101*, 3927.

(12) Huang, H.; Yang, S. H. *J. Phys. Chem. B* **1998**, *102*, 10196.

(13) Yamada, H.; Maruyama, T.; Akimoto, K.*Blue Laser Light Emitting Diodes II*, [*Int*,. *Symp.*] **1998**, 266.

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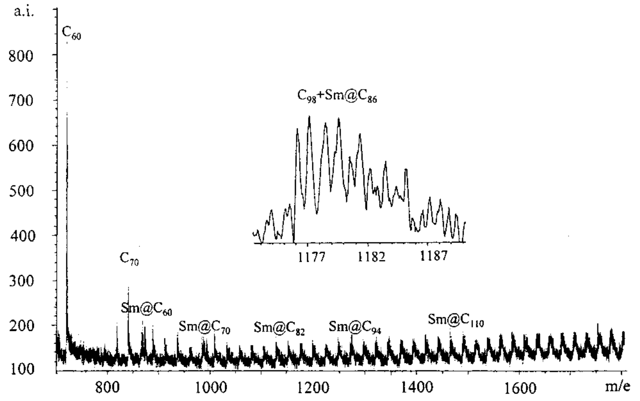

Figure 1. Positive ion MALDI-TOF mass spectrum of the primary soot.

of loose cathode deposit was obtained. The raw soot was collected under nitrogen and then successively extracted with a Soxhlet extractor by carbon disulfide and pyridine until there was nearly no discernible color. The solid obtained through rotary evaporation of the pyridine extract, after complete washing with diethyl ether, was then extracted with CS_2 and the extract thus obtained was combined with the CS_2 extract of the soot. The combined CS_2 extract, after concentration by a rotary evaporator, was fractionated through column chromatography on silica gel using petroleum ether, a 1:1 petroleum ether−toluene mixture and CS_2 as successive eluents. A toluene dispersion of the raw soot, the CS_2 and pyridine extracts, and the CS_2 eluates were respectively analyzed by MALDI-TOF mass spectrometry (BIFLEX III, Bruker Inc.). Radiation pulses (10^{-8} s) from a N_2 laser operating at 337 nm were used to desorb the species from a coated stainless steel plate, and the positive ions formed were detected in a reflection mode.

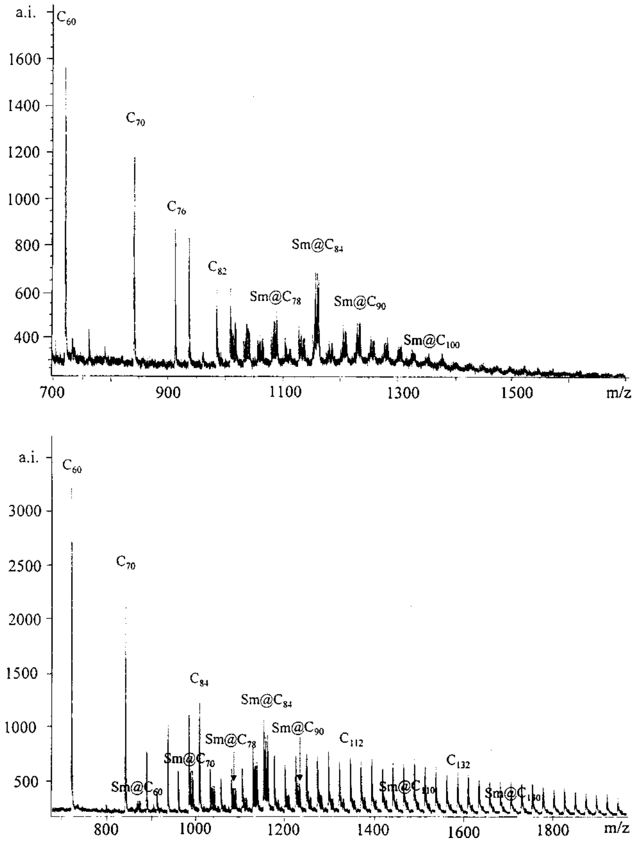

Figure 2. Positive ion MALDI-TOF mass spectra of (a, top) CS_2 and (b, bottom) pyridine extracts.

Results and Discussion

From Figure 1, the MALDI-TOF mass spectrum for the primary soot, a series of broad combined peaks of C_{2n+12} and Sm@C_{2n} ($2n \geq 60$) are observed. As the inset shows, the peaks of metallofullerenes broaden up to 10 amu due to the large distribution of seven isotopes of Sm (144, 3.16−2.87%; 147, 15.10−14.87%; 148, 11.35−11.22%; 149, 3.96−13.82%; 150, 7.47−7.36%; 152, 26.90−26.55%; 154, 22.88−22.43%).[14] In agreement with Moro et al.,[10] the lowest mass metallofullerene observed is Sm@C_{60}, which is adjacent to C_{72}, and no multimetallofullerenes are detected. In addition, Sm@C_{60} and Sm@C_{70} are the most abundant species. However, in our case, variation of the peak intensities for metallofullerenes at *m/e* higher than that of Sm@C_{70} is different. The relative intensity of metallofullerenes shown in the figure changes little instead of monotonically decreasing as a function of mass. Moreover, the peak height ratios Sm@C_{2n}:C_{2n+12} are much higher than that previously reported.[10] Thus, on the basis of the peak height ratios of metallofullerenes to their neighboring fullerene or to Sm@C_{60}, it is evident that the yield of Sm@C_{2n} is much increased with our improved procedure. Furthermore, many new Sm metallofullerenes, Sm@C_{62}, Sm@C_{64}, and Sm@C_{2n} ($2n \geq 100$) for example, were also found.

To obtain as many metallofullerenes as possible, the primary soot was successively extracted with CS_2 and pyridine. The MALDI-TOF mass spectra of the extracts after CS_2 extraction and pyridine extraction are shown in Figure 2a,b, respectively. From Figure 2a, it can be seen that a series of peaks assignable to Sm@C_{2n} ($2n \geq 72$) are observed with Sm@C_{84} as the strongest one. Figure 2b exhibits high peaks of Sm@C_{84}, Sm@C_{82}, Sm@C_{70}, Sm@C_{74}, Sm@C_{90}, and Sm@C_{78}. According to Figure 2, Sm endohedral fullerenes have been effectively extracted by CS_2 and pyridine. This high yield from the extraction is probably due to the high extracting power of CS_2 and pyridine toward these species as well as a high content of metallofullerenes in the soot. It should be noted that Sm@C_{84} is the most abundant species in either CS_2 or pyridine extracts, which is different from the finding of Gillan et al.,[9] who stated that Sm@C_{82} was the most abundant metallofullerene in the toluene extract. Since Sm@C_{84} is not more abundant than the other Sm@C_{2n} in the primary soot and Sm is assumed to be at +2 oxidation state in these metallofullerenes, $M^{2+}@C_{84}{}^{2-}$ are supposed to be easily extracted by CS_2 just as $M^{3+}@C_{82}{}^{3-}$ (M = Y, La, etc.).[15,16] In agreement with this supposition, the MALD-TOF mass spectra of Ca, Ba, and Yb endohedral fullerenes obtained by our improved method show similar results. It is interesting to note that, in contrast to the cases for $M^{3+}@C_{60}{}^{3-}$ and $M^{3+}@C_{70}{}^{3-}$ (M = La, Gd, and Dy, etc.),[11] Sm@C_{60} and Sm@C_{70} are effectively extracted by pyridine yet unable to be extracted by CS_2, as was observed for Ca@C_{60} and Ca@C_{70}.[17] According to Kubozono et al., $M^{3+}@C_{60}{}^{3-}$

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[14] Holden, N. E. *Pure Appl. Chem.* **1980**, *52*, 2349.

[15] Shinohara, H.; Sato, H.; Saito, Y. *J. Phys. Chem.* **1992**, *96*, 3571.

[16] Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67.

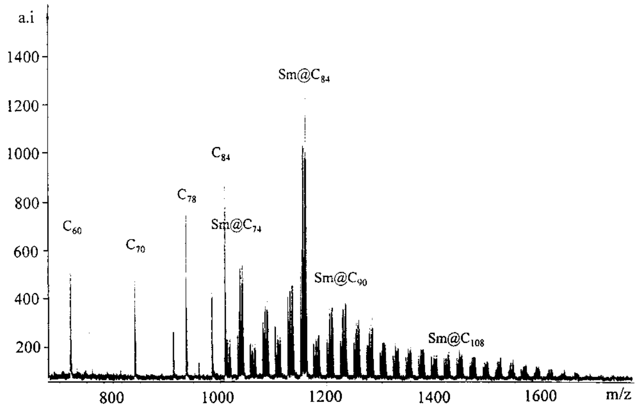

Figure 3. Typical positive ion MALDI-TOF mass spectrum of CS_2 eluate.

(M = Y, La, and Gd, etc.)[18] and $Ca@C_{60}$ (M = Ca and Sr)[19] can be easily extracted by aniline. To extract $Sm@C_{60}$ and $Sm@C_{70}$ selectively, after pyridine extraction, aniline was used to extract the residues. Unfortunately, $Sm@C_{60}$ and $Sm@C_{70}$ were not richer than any other $Sm@C_{2n}$ in the aniline extract. This exhibits the special solubility of $Sm@C_{60}$ and $Sm@C_{70}$, which might be a result of their special electronic structures. As for $Sm@C_{72}$ and $Sm@C_{76}$, they were almost nonexistent in the pyridine extract, indicating that they are either less soluble or unstable in pyridine.

On the basis of the above procedure, column chromatography was used to enrich the metallofullerenes, and the CS_2 fraction was collected. Figure 3 is a typical MALD-TOF mass spectrum of the CS_2 eluate. It shows the dominant peaks of $Sm@C_{84}$, $Sm@C_{74}$, $Sm@C_{82}$, $Sm@C_{78}$, $Sm@C_{90}$, and $Sm@C_{88}$. Since the peak intensity of $Sm@C_{84}$ is stronger than that of any empty fullerenes, it can be concluded that the high yields of Sm endohedral fullerenes were successfully enriched in the CS_2 eluate through column chromatography. These elution behaviors of fullerenes and metallofullerenes are consistent with their different solubilities in various solvents. Since metallofullerenes are assumed to have dipole moments similar to fullerenes that have nearly the same molecular mass, they are expected to have nearly the same adsorption power to silica gel and can be eluted together by CS_2.

The scarcity of research on Sm endohedral fullerenes is due to their low production yield and difficulty in isolation. The yield of rare earth metallofullerenes has been correlated with the ionization potentials,[12,20] the oxidation states[10,11] and ionic radii[11] of the encaged metals. In our opinion, the yields of metallofullerenes prepared by the dc arc discharge method are directly associated with the thermal properties of the encaged metals besides the factors mentioned above, especially their boiling points. According to Möschel and Jansen,[21] the temperature in an electric arc is as high as 5000−6000 °C. At such a high temperature, it is difficult to vaporize carbon and the encaged metal simultaneously as most of the encaged metal atoms are vaporized before the graphite carbon starts to sublime. Thus, we propose that the yields of metallofullerenes are directly proportional to the boiling points of the encaged metals. Shown in Figure 4 are the plots of the boiling points[22] of the lanthanide metals and the relative yields[12] of their endohedral fullerenes as a function of the encaged metal identities. From the figure, it can be seen that the two plots are very similar in shape except for some minor differences. For the metals Pr, Nd, Sm, and Eu, as well as Tb, Dy, Ho, Er, Tm, and Yb, both curves show exactly the same order. The boiling points of Sm, Eu, Tm, and Yb are the lowest, and so are the yields of their endohedral fullerenes. The exceptional elements are Ce, Tb, La, Gd, and Lu. According to Huang and Yang's report,[12] the yields of the Ce and Tb metallofullerenes are especially high, which might be due to the facile formation of $(CeC_2)_n$ and $(TbC_2)_n$ at high temperature. The relatively low yields of La, Gd, and Lu metallofullerenes might be associated with the high third ionization potentials of the metals, and the large ionic radii of La^{3+} might be another factor leading to this low yield just as in the case of Ca and Ba metallofullerenes.[23]

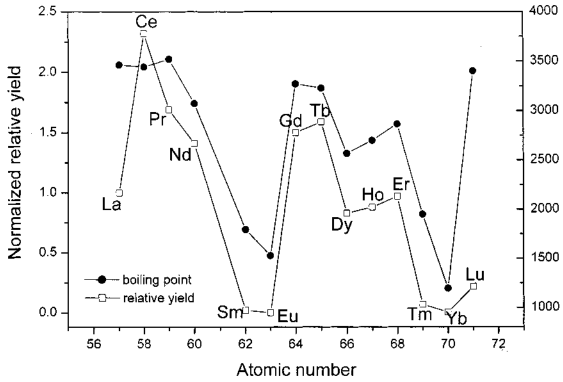

Figure 4. Boiling points of lanthanide metals and relative yields of their endohedral fullerenes.

To enhance the yield of metallofullerenes, two ways could be adopted. First, Sm_2Co_{17} alloy is employed instead of Sm_2O_3 as the encaged metal source. According to Tohji et al.,[24] the yield of CS_2 extract decreases about 90% when pure graphite anode was doped with M_2O_3 (M = Y, La, Gd, etc.). In contrast, when the graphite anode was doped with Sm_2Co_{17}, this yield only decreases to less than 30%, and the extract is richer in metallofullerenes. Because the disturbance of oxygen produced by reducing the metal oxide is avoided during the dc arc discharge process, the production yields of metallofullerenes are elevated. It is interesting to see the role of cobalt in the process of metallofullerene formation. Just as the inset in Figure 1 shows, no cobalt metallofullerenes have been found in our experiment. Moreover,

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(17) Kubozono, Y.; Ohta, T.; Hayashibara, T.; Maede, H.; Ishida, H.; Kashino, S.; Oshima, K.; Yamzaki, H.; Ukita, S.; Sogabe, T. *Chem. Lett.* **1995**, 457.

(18) Kubozono, Y.; Maede, H.; Takabayashi, Y.; Hiraoka, K.; Nakai, T.; Kashino, S.; Emura, S.; Ukita, S.; Sogabe, T. *J. Am. Chem. Soc.* **1996**, *118*, 6998.

(19) Kubozono, Y.; Noto, T.; Ohta, T.; Maede, H.; Kashino, S.; Emura, S.; Ukita, S.; Sogabe, T. *Chem. Lett.* **1996**, 453.

(20) Ross, M. M.; Nelson, H. H.; Callahan, J. H.; Mceivvany, S. W. *J. Phys. Chem.* **1992**, *96*, 5231.

(21) Möschel, C.; Jansen, M. *Chem. Ber./Recl.* **1997**, *130*, 1761.

(22) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*; ASM International: Metals Park, OH, 1973.

(23) John, T.; Dennis, S.; Shinohara, H. *Appl. Phys. A: Mater. Sci. Process.* **1998**, *66*, 243.

(24) Tohji, K.; Saito, K.; Jeyadevan, B.; Matsuoka, I.; Sogabe, T.; Nagasawa, K. *Fullerene Sci. Technol.* **1997**, *5*, 33.

up to the present no Co-containing metallofullerenes have been identified. Thus, it can be concluded that cobalt plays only the role of a catalyst just as in the process of single-walled carbon nanotube formation.[25] Moreover, the boiling point of Sm_2Co_{17} is so high that it is beneficial for samarium and graphite to be co-vaporized. In addition, the existence of cobalt in the anode makes it possible to maintain a wide gap between the electrodes without extinguishing the arc, as a result of its electric conductivity. This gap was found to be as long as 50 mm under our conditions.

Second, arc-discharging parameters can be so chosen to lower the temperature of the arc. In contrast with the conventional dc arc discharge conditions, higher helium pressure (720 Torr), lower electric current (50 A), wider gap distance (12 mm), and higher M/C molar ratio (0.05:the overall Sm/C) were employed in our experiment. Under such mild conditions, the arc temperature as well as the evaporation rate of the anode is lowered and the vaporized carbon and metal atoms would survive longer in the arc plasma region to collide with each other to form metallofullerenes. Apart from the temperature factor, the helium pressure has great influence on the production yield of metallofullerenes. When the same method was used to prepare Y-containing metallofullerenes, the production yield was elevated two times when the helium pressure was changed from 125 to 720 Torr according to the relative ratios in peak intensity of $Y@C_{82}$:C_{60} in the MALD-TOF mass spectra obtained. It is also meaningful to note the relationship between the yields of the metallofullerenes and higher fullerenes. Shinohara et al.[26] pointed out that the formation of C_{60} and metallofullerenes are competitive in their early stages. Suzuki et al.[27] also indicated that there is some correlation between the formation condition for higher fullerenes and that of $M@C_{82}$. During the arc discharge processes, we found that the yield of metallofullerenes is usually positively correlated to that of their corresponding fullerenes.[28] This finding lead us to dope the composite anode with SiC to enhance the formation of higher fullerenes,[29] since the carbon cages being capable of encaging metal atoms are usually the higher ones. Though C_{60}- and C_{70}-based metallofullerenes are very rich in the raw soot, they are difficult to be extracted by common organic solvents.

Conclusions

In summary, an improved dc arc discharge method for high-yield preparation of Sm-containing metallofullerenes $Sm@C_{2n}$ ($2n \geqslant 60$) has been developed by optimizing the arc-discharging parameters and employing a Sm_2Co_{17} alloy in place of Sm_2O_3 as the encaged metal source. Through two-stage successive extraction with CS_2 and pyridine, the extraction yield is also improved. We found that, in contrast to other rare earth metallofullerenes based on C_{60} and C_{70}, $Sm@C_{60}$ and $Sm@C_{70}$ show special solubility in pyridine. Application of column chromatography on silica gel allows us to enrich metallofullerenes conveniently, and the enriched sample thus obtained facilitates further isolation of pure $Sm@C_{2n}$ by HPLC.

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Supporting Information Available: Figures of the positive-ion MALDI-TOF mass spectrum of CS_2 extract from the soot containing Y endohedral fullerenes prepared at 125 and 725 Torr helium pressure and containing Ca endohedral fullerenes (PDF). This material is free of charge via the Internet at http://pubs.acs.org.

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(25) Bethune, D. S.; Kiang, C. H.; deVries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.

(26) Shinohara, H.; Saito, H.; Saito, Y.; Ohkochi, M.; Ando, Y. *J. Phys. Chem*. **1992**, *96*, 3571.

(27) Suzuki, S.; Wakabyyashi, T.; Yohji, A. *Electrochem. Soc. Proc.* **1995**, *10*, 740.

(28) Lian, Y. F.; Shi, Z. J.; Zhou, X. H.; He, X. R.; Gu, Z. N. *Carbon*, in press.

(29) Cao, B. P.; Zhou, L. Q.; Shi, Z. J.; Zhou, X. H.; Gu, Z. N.; Xiao, H. Z.; Wang, J. Z. *Carbon* **1998**, *36*, 453.